One-Pot Synthesis of CeO_2 NC-Superlattices

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Electronic Supplementary Information (ESI)

Experimental Section

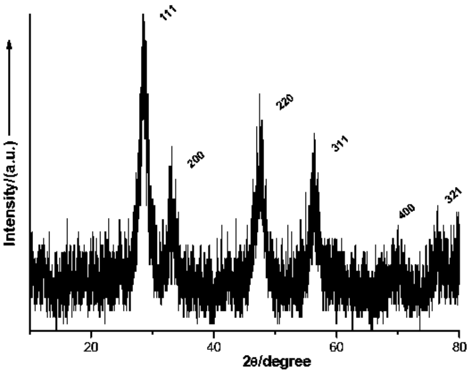
All chemicals were of analytical grade and used as received without further treatment. Deionized water was used throughout.

In a typical synthesis, 0.5g NaOH was added to the mixture of 4ml oleic acid (OA) and 15ml ethanol, and stirring vigorously for a while to form a clear solution. 8~15mmol (NH4)2Ce(NO3)6 were dissolved into 5-10ml of distilled water, and then, added into above solution by drops. After stirring for a while, additional 5ml ethanol was added, and both the mixed-solvent and generated precipitation were all transferred into a 40ml autoclave. Sealed the autoclave and heated it at 120℃~160℃ for 6~24hours. The system was then allowed to cool to room temperature. The final products were spontaneously separated in the bottom of the autoclave. Colloidal Particles CeO_2 with superlattice structures were prepared as above, except that more (18mmol~) $(NH_4)_2Ce(NO_3)_6$ was added and heated for 24h~36h at 180℃.

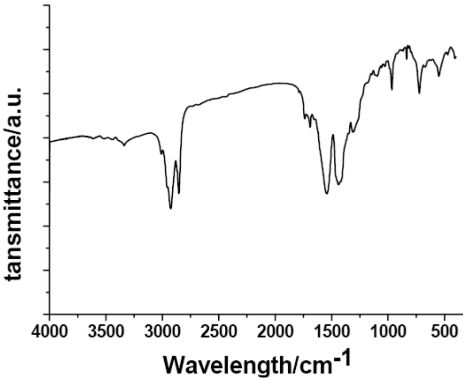
The products were characterized by a Rigaku. D/max 2500Pc X-ray diffractmeter (XRD) with Cu Kα radiation (λ=1.5418Å). The operation voltage and current were kept at 40KV and 250mA, respectively. The 2θ range 10°-80° was used in steps of 0.3° with a count time of 2s. The sizes and morphologies of the NCs were examined with a JEOL JEM-1200EX transmission electron microscope (TEM) and a Tecnai F20 high-resolution transmission electron microscope (HRTEM). SAED patterns were recorded by transmission electron microscopy. Fourier transform infrared spectra (Perkin-Elmer Spectrum GX) were used to characterize the structure of the samples. Energy dispersion X-ray analysis (EDXA) measurement was performed with a Gantan parallel detection spectrometer attached to transmission electron microscope. Thermogravimetric analysis (TGA) was recorded by TA instruments TGA2050. UV-Vis spectrum was taken by Uv-Vis diffuse-reflectance spectroscopy (Shimadzu UV-2100s spectrophotometer)

The catalytic activities for CO oxidation were evaluated in a fixed-bed quartz tubular reactor. The catalyst samples (0.25g) were placed in the reactor after annealed at 400℃ for 2h and dispersed in 35ml distill water firstly. 1ml of 1% $HAuCl_4 \cdot 4H_2O$ (weight ratio) was added into above solution by drops and the pH was kept at 9. Finally, the catalyst was collected by centrifugation and dried at 160℃ for 10h. The reactant gases (1.00% CO, 16.00% O_2, balanced with nitrogen) went through the reactor at a rate of 100ml/min. The composition of the gas existed in the reactor was monitored by gas chromatography (Shimadzu GC-8A)

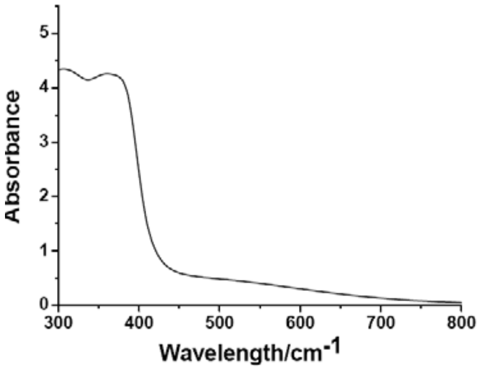
The powder X-ray diffraction (XRD) measurement on CeO_2 NCs agrees with bulk materials perfectly. No peaks of any other phases or impurities were detected. The apparent broadening of some peaks indicates small size of the as-obtained NCs. By Scherrer equation ($d=0.89\lambda/B\cos\theta$), calculated size of the products is ca. 4.1 nm, which is quite close to the corresponding result measured from TEM image.



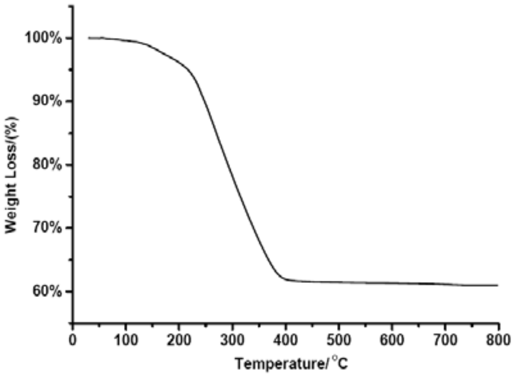
FT-IR spectrum of CeO_2 NCs, 2919cm^{-1} and 2856cm^{-1} are attributed to the symmetric and antisymmetric methylene stretches. 1542cm^{-1} and 1438cm^{-1} are assigned to the antisymmetric νs (COO-) and the symmetric νs (COO-) stretches.[1]



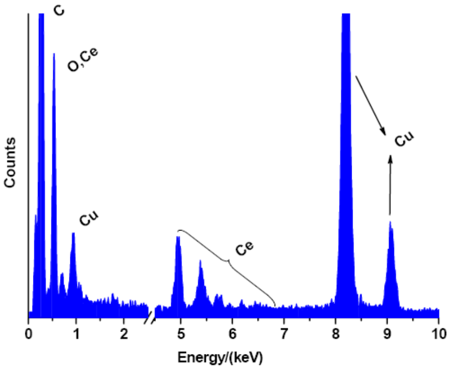
Uv-Vis absorption spectrum of CeO_2 NCs (disperse in cyclohexane).



Thermal gravity (TG) curve of the samples measured under atmosphere



Energy dispersion X-ray analysis (EDXA) of the CeO_2 NCs. (Cu signal rose from the copper grid. C signal rose from the carbon membrane and OA molecules which absorb on the surface of the NCs)



TEM images of as-obtained irregular colloidal particles with superlattice structures (Fig S2a), which are assembled by CeO_2 NCs spontaneously. These colloidal particles were obtained directly in the synthetic process without further treatments, and moreover, the as-obtained colloidal particles will be separated to dissociated NCs gradually (fig S2b), when disperses them into cyclohexane (15~20mg/ml) and ultrasonic treated for 0.5~1h at 200W.

Fig S2a

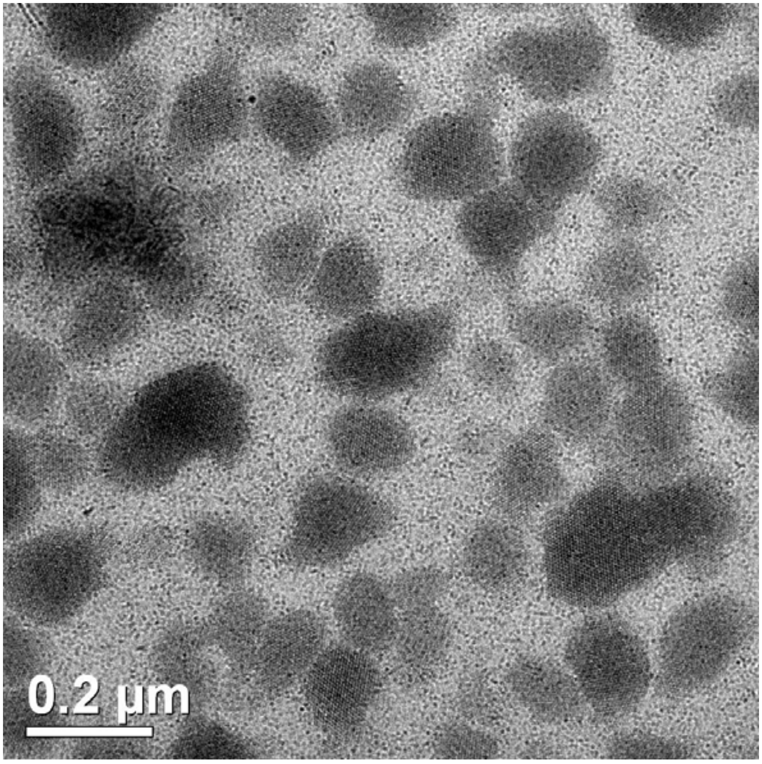
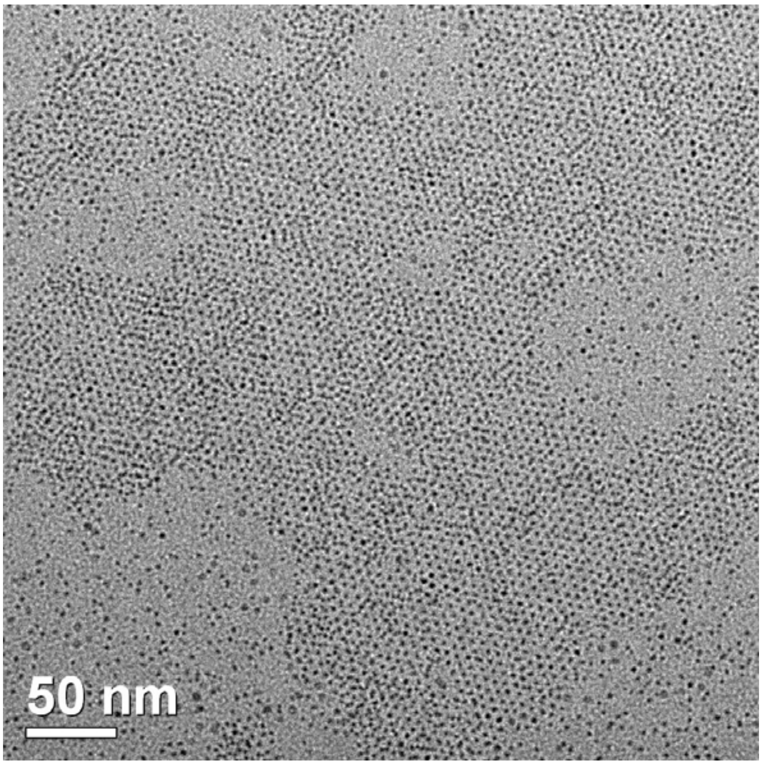


Fig S2b



TEM image of CNTs knitted networks (Fig S3a) and CeO_2 NCs assembled membrane (Fig S3b)

Fig S3a

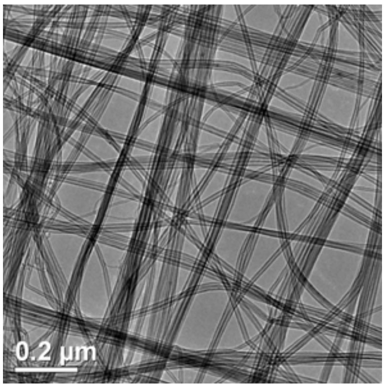
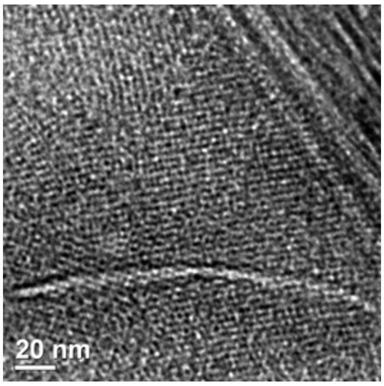
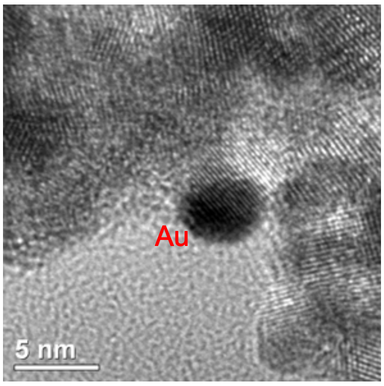


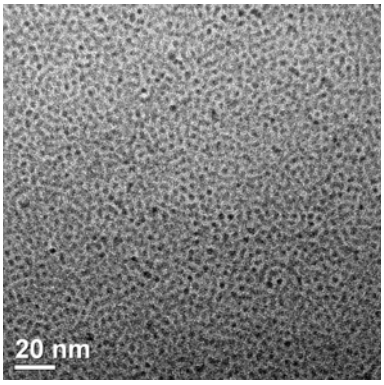
Fig S3b



TEM image of catalyst (CeO2/Au 2％)



TEM images of $Ce_xZr_{1-x}O_2$ NCs synthesized by the same strategy.[2]



Structures of $Ce(NO_3)_6^{2-}$ and Schemes of the icosahedral crystal structure and the synthesis

The crystal structure of $Ce(NO_3)_6^{2-}$, as shown in following figure, has been widely reported in previous reference[3] and inorganic handbook[4]. Due to this crystal structure, the corresponding $Ce(NO_3)_6^{2-}$ will be destroyed in strong acid conditions (such as $HClO_4$). But in our system, the pH will almost keep around 6.7 during the whole process. So, we proposed that the Ce^{4+} in

$Ce(NO_3)_6^{2-}$ will be more stable than the bare Ce^{3+} or Ce^{4+} in aqueous solution. Furthermore, when we used $CeCl_3$ or $Ce(SO_4)_2$ as precursor instead of $(NH_4)_2Ce(NO_3)_6$ for the synthesis of CeO_2 NPs, the products were always irregular CeO_2 nanoparticles with broad size distribution. Based on these as-mentioned theoretical and experimental evidences, we propose a probably mechanism as in the following fig with great prudential.

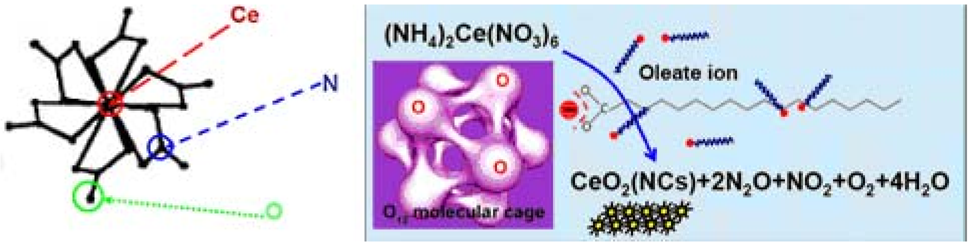


Fig. Schemes of the icosahedral structures of $Ce(NO_3)_6^{2-}$ crystal and the synthesis process

References

1. F Soderlind, H Pedersen, R. M Petoral, P. O Kall, K, J. Uvdal, Colloid and Interface Sci 2005, 288, 140.
2. Z.Y Huo and Y.D Li, $Ce_xZr_{1-x}O_2$ NCs and assembled porous materials: Promising Catalysts for CO oxidation, (submitted).
3. N. Guillou, Acta Crystallographica Section C-Crystal Structure Communications 1995, 51, 1029.
4. G. A. Bandurkin and B. F. Dzhurinskii A 10-APEX POLYHEDRON OF IMPORTANCE IN THE CRYSTAL CHEMISTRY OF THE RARE EARTH ELEMENTS